

Effects of Epoxidized Palm Oil (EPO) on Mechanical Properties of Polyhydroxyalkanoates (PHA)

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Abstract:

Plastics are the most popular material for conventional usage especially in packaging application. However, this material becomes problematic when it reaches the disposal stage. Most of them can take almost hundreds or even thousands of years to degrade. Thus, biodegradable materials, for instance polyhydroxyalkanoates (PHA), are the best option to replace conventional plastics. The PHA are varied from 1 to 5 wt% epoxidized palm oil (EPO) loading and the structure and mechanical properties are studied through thermal, chemical, morphology and mechanical analysis. FTIR spectra and DSC thermogram show good compatibility between EPO loading and PHA matrix. 3 wt% EPO gives the best improvement in terms of tensile strength, modulus tensile, flexural strength and flexural modulus with improvements around 331%, 281%, 294% and 300% respectively compared to the performance of neat PHA. SEM micrographs also reveal that the homogenous dispersion of EPO loading into PHA matrix at 1, 2 and 3 wt% of PHA. The addition of EPO loading in the PHA matrix makes stress transfer from matrix to plasticizer (EPO) and increases the chain mobility PHA which results in high flexibility and stiffness.

Keywords: biodegradable, epoxidized palm oil, polyhydroxyalkanoates, plasticizer

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I. INTRODUCTION

Conventional plastics make quality of human's life in terms of packaging material improve by shifting current material such as paper and glass. Although the conventional plastics are known as non-biodegradable, they have some unique properties such as high toughness, light and durable. Association of Plastic Manufacturers reported that plastic production increased as much as 3.9% in the year 2013 (which carried the value around 299 million tons) compared to the year 2012[1].

However, non-biodegradable properties of conventional plastics often raise serious concerns in the society and have eventually become an issue worldwide. The degradation duration of plastics depends on their type but the average duration for plastic bottles to degrade is at least around 450 years. Some bottles may even take 1000 years to degrade completely. The worst case is that bottles with Polyethylene Terephthalate (PET) base will never degrade[2]. Moreover, food packaging covers two-thirds of the total packaging waste by volume

and this is due to the fact that each person consumes food at least three times per day[3]. On the other hand, the decline of the supply of fossil fuel over the years is another cause for scientists to explore and establish alternative methods for the manufacture of biologically based polymer for the survival of human life.

Besides, polyhydroxyalkanoates (PHAs) can be perceived as the most popular material among the various groups of biopolymers. PHAs are known to be biodegradable, thermoplastic, biocompatible and non-toxic. PHA is synthesized by various bacteria in the form of carbon and energy storage compounds such that final product is polyester of hydroxy alkanoates (HAs). PHAs can be categorized into two main types which are short chain length PHA (scLPHA) and medium chain length PHA (mcL PHAs). The classification of PHAs depends on the number of carbon atoms in the monomers[1].

The first discovered PHA component, polyhydroxybutyrate (PHB), has been used in packaging materials and small disposable products.

A study comparing the performance of food packaging with PHB and polypropylene (PP) shows that PHB has a 50 percent lower value of deformation. This suggests that PHB is less flexible and stiffer than PP. While, at high temperatures, PHB shows better quality than PP. PHB's equivalent performance makes it ideal for high-fat food packaging. It can also withstand low temperatures such as storage of sour cream and high temperatures such as microwave[4]

Adding plasticizer to the polymer is said to be an easy way to enhance polymer's thermal and mechanical properties[5]. Epoxidized vegetable oils (EVO) are useful additives to improve PHA's mechanical properties. For example, epoxidized palm oil is a material that is renewable and environmentally friendly, making it the best way to be added to PHA. In addition, this low-cost material acts in the composite application as a good cost reduction option by partially replacing epoxy resin. Therefore, the use of modified EPO as part of the consummate epoxy systems improves mechanical properties and curing characteristics[6].

Bioplastic may be biologically or biodegradable. Renewable resources receive biodegradable polymers. It requires a process of biodegradation in which it can return to the natural state[7]. This process occurs when enzymes and chemical decomposition react with living organisms such as pillows and biodegradation occurs along the course[8].

Rapid development of biodegradable polymers studies will bring promising benefits to the use of fossil-based raw materials and ways to overcome the problem of conventional plastics at disposal. Biopolymers are an advantage in lowering CO₂ emissions and are a key factor in the continuous development of biopolymers. Unfortunately, when they reach a high production range, the biodegradable polymers face some disadvantages. Poor performance, production speed, production costs and lack of infrastructure are some of the challenges the industry faces when it comes to biodegradable polymers[9].

In order to study and enhance the thermal and mechanical properties of PHA, numerous studies have been carried out. It is expected that all the studies will take PHA to the current market for

commercial exploitation. Similar PHA have been detected. However, there are only four types that achieved a large scale of production and they are poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHHx), poly[(R)-3-hydroxybutyrate] (PHB), poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate] (P3HB4HB) and poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] (PHBV)[10]. Production of PHA begins with fermentation followed by separation of biomass, drying, extraction and ending with PHA packaging[11].

Biodegradable polymers have been estimated to consume about 50 million kilograms per year in the European region. Nevertheless, the production of biopolymers is still small compared to the annual production of polymers, which is about 1% and is equal to about 100 million tons. Because of the high production costs, low-grade applications of food packaging biopolymers are commonly used[12].

In this study, we melt blended PHA with different EPO loading in a range of 1 to 5 wt% to correlate the effect of stated EPO loading on the tensile and flexural performances of PHA. Chemical composition, thermal properties and morphology structure also were studied, and optimal composition of PHA/EPO blends was identified.

II. MATERIALS AND METHODS

A. Materials

Biodegradable polymer used for this study is polyhydroxyalkanoates (PHA). PHAs were purchased through international suppliers namely, from Shenzhen Bright China Industrial Co. Ltd., China. The plasticizer used in this study is epoxidized palm oil (EPO). The EPO was provided by the Malaysian Palm Oil Board (MPOB).

B. Preparation of PHA/EPO Blends

PHA/EPO blends were prepared by melt blending technique using Brabender Internal Mixer at 175 °C for 15 minutes with 50 rpm of rotor speed. The weight of EPO studied is varied between 1 to 5 wt%. After melt blending, the sheets for each EPO loading with 1mm and 3 mm thickness for tensile test and flexural test respectively were prepared by using hydraulic hot-press with a pressure of 110 kg/cm³ at

175 °C for 8 minutes. The sheets or samples were then left to cool at room temperature.

C. Fourier Transform Infrared (FTIR) Spectra

The FTIR spectra of neat PHA, neat EPO, and PHA/EPO blends were recorded by Thermo Scientific (Model: NICOLET iS50). This chemical analyser has been equipped with purpose-built accessories and integrated software. The spectra were recorded and the frequency ranges from 280 cm^{-1} to 4000 cm^{-1} .

D. Differential Scanning Calorimetry (DSC)

A DSC analyser, Mettler Toledo, was used to perform melting and crystallization behaviour testing for each blend. The scanning process was carried out at the rate of 10 °C/min from -60 to 200 °C with a flow rate of nitrogen gas of 50 mL/min. The method used differential heat flow and temperature, typically related to the transition in materials.

E. Tensile Test

The tensile test was conducted using Shimadzu Universal Testing Machine based on ASTM D638. The test was carried out at a constant 5 mm/min crosshead speed, 1 kN load cell 10 mm gauge length. From the stress-strain data obtained, the evaluations of tensile strength, tensile modulus, and elongation at break were done. Five dumbbell shaped samples for each composition were prepared to make sure that a reliable mean and standard deviation can be obtained.

F. Scanning Electron Microscopy (SEM)

The morphology of plasticized PHA with different EPO loading is analysed under SEM at room temperature. The brand used for SEM is JEOL (model JSM-6300F) with field emission gun and accelerating voltage of 7 kV. Before the samples are characterized by SEM, the surface of the sample is coated with a few nanometres palladium (Pd) coating. The analysis of morphology was carried out on the fracture surface of failed tensile sample.

G. Flexural Test

The flexural test was carried out using Shimadzu Universal Testing Machine in accordance with ASTM D790. The test was prepared at a constant crosshead speed of 3 mm/min and load cell of 1kN. Seven samples for each composition with the dimension of 127.00 mm x 12.70 mm x 3.00 mm were prepared. Flexural strength and flexural

modulus were obtained. An average of five readings for each composition was calculated.

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared (FTIR) Spectra

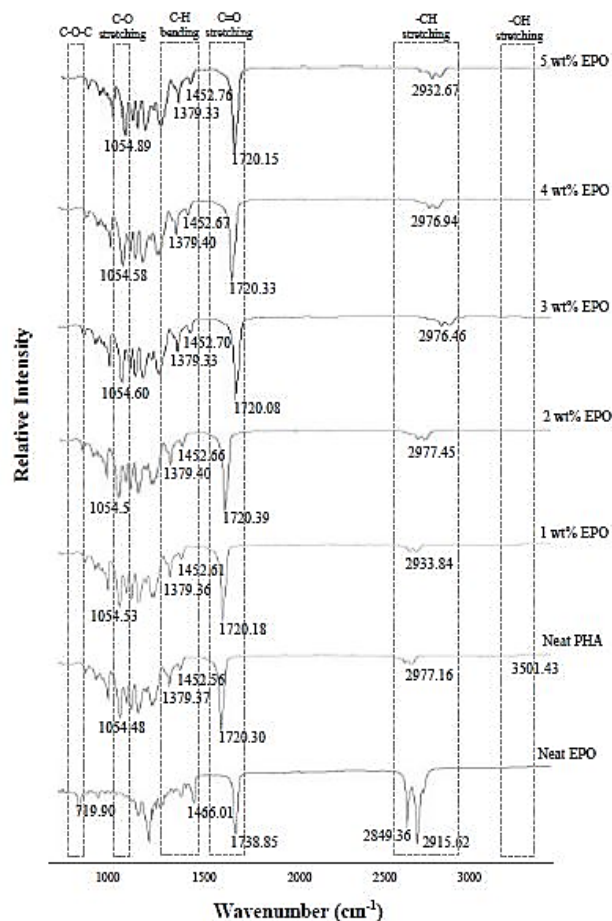


Fig. 1. FTIR spectra for neat EPO, neat PHA and different EPO loading varies from 1 to 5 wt%

FTIR spectroscopy is used to determine the molecular interaction between epoxidized palm oil (EPO) with polyhydroxyalkanoate (PHA). It is indeed true that molecules vibrate. The vibration of molecules is changed when FTIR spectroscopy absorbs photons of the appropriate energy. Thus, it can identify a functional group for specific regions by monitoring the absorption peak shift. Fig. 1 shows the FTIR spectra and characteristic peaks of neat PHA, neat EPO, and PHA/EPO blends. Each composition shows four main regions which are -CH stretching, C=H stretching, C-H bending and -C-O stretching. FTIR spectra for EPO shows unique peaks behavior of C-O-C stretching that resulted in oxirane vibrations.

Epoxidized oils such as EPO are made up of oxygen (OOC) content[13]. The OOC influences the existence of hydrogen bonding between PHA and EPO. Another factor includes the creation of hydrogen bonding that is, the interaction between polymers with a plasticizer. Effective plasticizer consists of two types of polar and non-polar structural components[14]. Other than the carbonyl group of carboxylic ester functionality, the OOC can also be presented as a polar component. The OOC value indicates the strength of interaction between PHA and EPO. A higher OOC value results in stronger interaction between the blends. Polar components of plasticizer create good compatibility with polymers and improve mechanical properties [13].

B. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a useful tool to study the thermal transition of these blends by examining the behaviour of glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). The plasticizer, for instance EPO, is expected to lower down the T_g so that mechanical properties of the polymer can be enhanced[15]. Fig. 2 shows DSC thermogram for each composition.

Moreover, DSC also reveals the T_m behavior of the PHA. The endothermic peak of melting, T_m , for neat PHA is at 175.4 °C. There is a slight decrease in the melting temperature for all PHA blends that ranges between 0.1 to 0.5 °C. Thus, the addition of plasticizer to the polymeric matrix does not affect the melting temperature greatly.

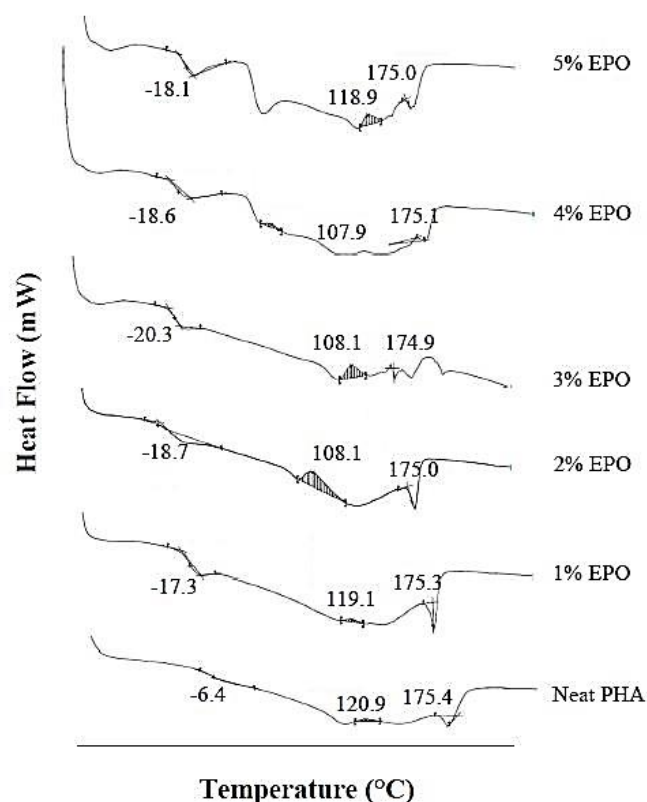


Fig. 2. DSC thermogram of neat PHA and PHA/EPO blends. Besides, cold crystallization temperature, T_c for neat PHA, 1, 2, 3, 4 and 5 wt% EPO are located at 120.9 °C, 119.1 °C, 108.1 °C, 108.1 °C, 107.9 °C and 118.9 °C, respectively. T_c for all PHA blends are lower than neat PHA. Cold crystallization encourages the spherulite nucleation which leads to shorter crystallization time and smaller spherulite size[9]. Therefore, small spherulite size reduces the brittleness of polymer. The decrease of T_c indicates that EPO is compatible with PHA. The results also show that the crystallization peak for 2 and 3 wt% of EPO were narrowed. It indicates that the ability of PHA to crystallize is increased.

Moreover, glass transition temperature, T_g of neat PHA is -6.4 °C. The addition of EPO into PHA network decreases the T_g to -17.3, -18.7, -20.3, -18.6 and -18.1 °C for 1, 2, 3, 4 and 5 wt% of EPO respectively. Plasticized PHA with 3 wt% EPO loading has the lowest T_g which leads to the notion that 3 wt% EPO loading is the optimum composition of PHA blend to enhance mechanical strength. Nevertheless, plasticized PHA for all compositions have lower T_g than pristine PHA due to the plasticization effect of EPO[9]. The decrease of T_g suggests that soft segments of EPO is mixed into hard segments of PHA. Therefore, the plasticization effect

improves the segmental mobility of PHA chains. This

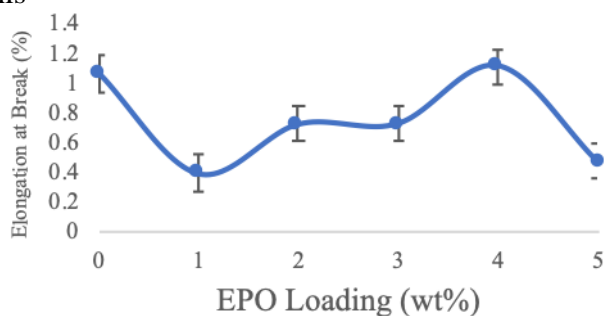


Fig. 4. Elongation at break of PHA blends

indicates that the EPO has good compatibility with PHA.

C. Tensile Test

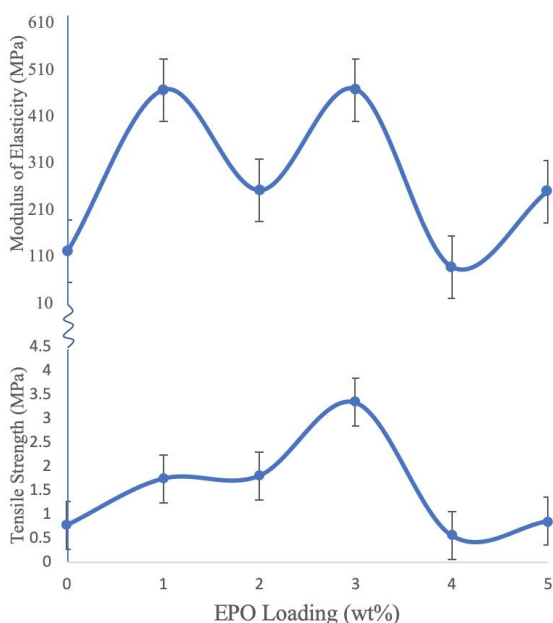


Fig. 3. Tensile properties of different PHA/EPO compositions

Tensile properties are examined in three main performances which are tensile strength, tensile modulus (modulus of elasticity) and elongation at break. All three performances are carried out at room temperature, 25 °C. The results of tensile strength and modulus of elasticity and elongation at break are shown in Fig. 3 and Fig. 4 respectively.

The addition of 1, 2 and 3 wt% of EPO shows significant improvement in the tensile strength by approximately 125%, 133% and 331% respectively. The addition of 3 wt% of EPO shows the highest improvement in the tensile strength of PHA. It can be said that EPO which functioned as a plasticizer has increased the interaction at the boundaries between

PHA matrix and EPO and it further improves the flexibility of the PHA blends. It also indicates that aggravated EPO is distributed homogeneously between PHA chains. This leads to high interphase interaction. Later, the tensile strength decreases as EPO loading increases[6].

Apart from that, a rapid decrease of tensile modulus is observed when the addition of EPO loading is greater than 3 wt%. It shows that the PHA blend has minimum amount of interfacial saturation for EPO in the interphase. Thus, based on the result of the tensile modulus, the optimum plasticizer amount that can be considered as the most efficient in stiffening PHA is 3 wt% of EPO.

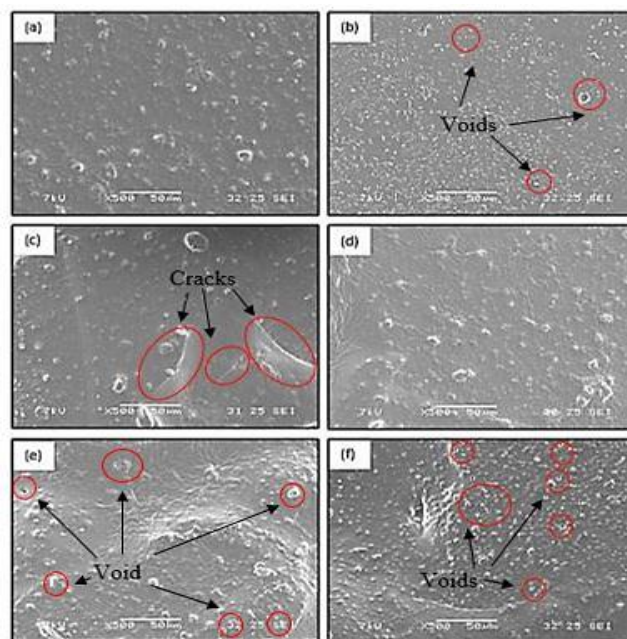


Fig. 5. Surface morphology for (a) Neat PHA; (b) 1 wt% EPO; (c) 2 wt% EPO; (d) 3 wt% EPO; (e) 4 wt% EPO; (f) 5 wt% EPO

Besides, 1 wt% of EPO records the lowest value of elongation at break while 4 wt% of EPO produces the highest value of elongation at break of PHA blends. The elongation at break decreases at 5 wt% of EPO loading. According to previous findings[6], weak points are created from free chain ends which result in micro voids therefore decrease the elongation at break. Plasticizer that has been infused in polymer matrix functions to overcome that brittleness. In this study, the presence of EPO as plasticizer increases the chain mobility of PHA and decreases the molecular interaction. Therefore, it is capable of enhancing the extensibility and flexibility of the PHA/EPO blends[13]. In conclusion, higher EPO loading leads to higher elongation at break with lower tensile strength.

D. Scanning Electron Microscopy (SEM)

Surface morphology of fractured surface of the tensile samples were examined by using scanning electron microscopy (SEM). This technique can also verify dispersion behaviour of EPO loading in the matrix of PHA qualitatively. Fig. 5 shows the SEM micrograph for all blends.

Fig. 5(a) displays PHA's common surface of brittle fracture. Fig. 5(b) shows very little defect cavities while cracks resulted from tensile force is shown in Fig. 5(c). Fig.

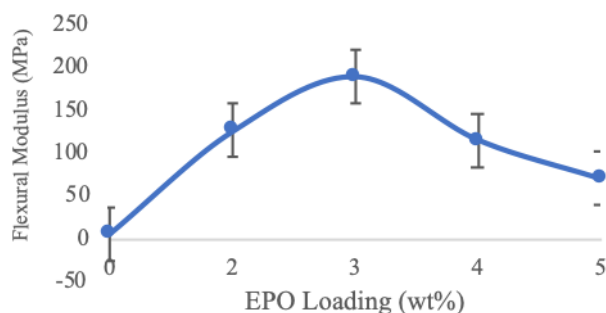


Fig. 7. Effect of EPO on flexural modulus of PHA

5(d) illustrates no sign of brittle fracture and defects cavities. Fig. 5(b) to (d) shows no existence of fibril and good compatibility as well as homogenous distribution within the PHA blends. The 1, 2 and 3 wt% of EPO successfully produced single phase morphology with a good adherence between particles of polymer-plasticizer interface[16]. Good compatibility leads to high efficiency of load transfer under stress environment.

Nevertheless, Fig. 5(e) and (f) reveals similar behaviour of surface morphology with the existence of empty micro voids all over the surface due to debonding. The micrographs also display poor adherence within the interface. The existence of micro voids in the blends suggests that there is a formation of

rich phase of EPO in the PHA matrix. Thus, phase separation and tendency towards the formation of micro voids increase as the EPO loading increases. In addition, the SEM micrographs prove that the homogeneity of the EPO loading dispersion is higher with lower EPO loading. This supports the mechanical performance of PHA blends.

E. Flexural Test

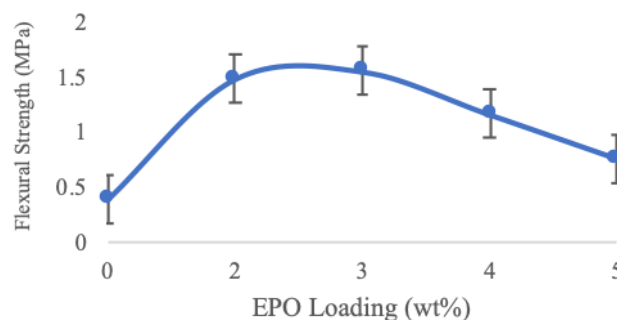


Fig. 6. Effect of EPO on flexural strength of PHA

Flexural test measures the strength of material to withstand tension and compression concurrently. The results for flexural strength and flexural modulus are shown in Fig.6 and Fig. 7, respectively. The trend from the performance of PHA blends is similar for both properties; the performance increased as the EPO loading content increased. However, at certain composition of EPO loading, the performance starts to drop.

All the PHA blends succeeded in improving the flexural strength regardless percentage of improvement. Flexural strength for 1 wt% of EPO is expected to have a value between 0.398 to 1.498 MPa. Furthermore, 3 wt% of EPO has the highest improvement compared to other PHA blends which carry the value of 1.567 MPa. Likewise, flexural modulus properties have similar pattern with flexural strength. 3 wt% of EPO gives the best improvement that is approximately 300% from neat PHA. The flexural modulus experiences a decrease when the addition of EPO loading is greater than 3 wt%. However, all the PHA blends showed improvements in the flexural modulus.

The enhancement of intermolecular interaction between EPO and PHA matrix leads to better flexural properties. Good intermolecular interaction makes stress transfer from the matrix to the plasticizer more efficient. Hence, the material requires more stress to failure which lead to better flexural strength. Apart from that, the formation of empty micro voids may affect the local stress on the PHA blends. Hence, it may affect the flexural properties of the blends. In addition, excess content of the EPO within PHA matrix reduces the stiffness of the matrix[17]. This also affects the decrease of flexural performance greater 3 wt% of EPO.

IV. CONCLUSION

All samples have been produced successfully by using the melt blending technique. There are six samples; neat PHA, neat EPO, PHA/1 wt% EPO, PHA/2 wt% EPO, PHA/3 wt% EPO, PHA/4 wt% EPO and PHA/5 wt% EPO. FTIR revealed that there is an interaction between oxirane group of EPO with a terminal hydroxyl group in the main chain of PHA which yields hydrogen bonding. This shows that there is an existence of hydroxyl group stretching in neat PHA at the peak of 3500 cm^{-1} . However, the characteristic peak disappeared as the neat PHA was plasticized with EPO. DSC also showed good compatibility between EPO and PHA and T_g of the blends were succeeded to be lowered. SEM micrographs proves that the EPO loading at 1, 2 and 3 wt% dispersed homogeneously with PHA matrix with no presence of empty micro voids and fibril which indicates that there is a good interfacial adhesion and compatibility between polymer-plasticizer. Nonetheless, PHA/4 wt% EPO and PHA/5 wt% EPO revealed poor adherence within the interface. Last but not least, 3 wt% of EPO performed excellent result for each mechanical test including tensile strength, tensile modulus, flexural strength and flexural modulus. Therefore, PHA/3 wt% EPO is the optimum composition in improving the mechanical properties of the PHA.

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