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Plasticizing Effects of Epoxidized Palm Oil on Mechanical and Thermal Properties of Poly(3-hydroxybutyrate-co-hydroxyvalerate)/Poly(caprolactone) Blends

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Poly(hydroxybutyrate-co-valerate) (PHBV), a biodegradable thermoplastic polymer, has attracted much attention because of increasing interest in protection of environment. PHBV is brittle, thus has restricted application. Improvement of its toughness has been attempted by blending poly (caprolactone (PCL). In this study, PCL helps in improving elongation at break and impact properties of PHBV. PHBV/PCL blends were blended using internal mixer. Differential scanning calorimetry (DSC) was used to determine the thermal properties of the blends and tensile and impact test for the mechanical test of the blends. There are two melting peaks shown in the DSC data of PHBV/PCL due to melting of PHBV and PCL. 60/40 ratio of PHBV/PCL was chosen as the optimum composition as it showed the highest elongation at break with 4.2 % improvement compared to pure PHBV. This blend ratio also has the lowest melting temperature of PHBV among ratio studied. Although the properties of PHBV/PCL blends were better than those of neat PHBV, the immiscibility of PHBV and PCL shown from DSC results inhibits further improvement of the properties of the blend. To improve the miscibility of the blends, 1 phr of epoxidized palm oil (EPO) was added to 60/40 blends. EPO has been proven to act as a plasticizer that increased the elongation at break and impact strength of the PHBV/PCL blends. This indicates that although both PHBV and PCL blends are not fully miscible, interaction exists between PHBV, PCL and EPO.

1. Introduction

Traditional plastics take a longer time to decompose, causing problems to the environment. To date, the required high energy and cost to recycle plastic waste is among the crucial environmental issues. In order to minimize these problems, biodegradable polymers have received significant attention due to their biodegradable properties. The biodegradable polymer, which are biosynthetic polymers and natural polymers, can be classified according to method of preparation. Biosynthetic polymers such as poly(hydroxybutrate) (PHB) is the most extensively used and studied biopolymer from poly(hydroxyalkanoates) (PHAs) family. PHB is an aliphatic polyester that is synthesized by bacterial fermentation. It helps in improving the environment especially in reducing plastic waste (Chun and Kim, 2000). There are some drawbacks that limit the potential properties of PHB. As it is produced by the fermentation of microorganisms, the production cost is higher as compared with other biodegradable polymers. It is also classified as a low thermal stability polymer that is brittle (in glass transition temperature range) with high crystallinity and easily to degrade above melting temperature. All these drawbacks hinder the homopolymer applications. Previously, to improve the properties of PHB, a various copolymer with different aliphatic polyester units have been biosynthesized. Poly(hydroxybutyrate-co-hydroxy- valerate) (PHBV) is one types of copolymer of PHB (Bal et al., 2019). With the incorporation of 3-hydroxyvalerate (3HV) unit into the PHB crystal structure, the crystallization process not only slowed down markedly, and melting temperature began to decrease, and the polymer attained better tensile strength (Sankhla et al., 2010). PHBV, copolymer of 3-hydroxybutyrate (3HB) and 3HV, has more potential in biomedical and industrial applications than PHB. Additionally, it also demonstrates that the 3HV content plays a critical role in the physical properties of PHA polymers (Bal et al., 2019). There are several

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shortcomings to the commercial use of PHBV. Blending of polymers is the most effective method to enhance the properties of polymer matrix and an innovative way to synthesize new bio-based polymer matrix with desirable properties with low cost method. Even though it is the improved version of PHB, it has poor thermal stability and fragility properties. These shortcomings narrow the utilization of PHBV. According to previous studies, there are different alternatives used in order to improve the performance of PHBV. Incorporation of nanofibrillated cellulose (NFC) and PHBV using solution casting method improved tensile modulus and crystallization of PHBV/NFC nanocomposites (Srithep et al., 2013). Addition of plasticizers such as polyethylene glycol (PEG), triethyl citrate (TEC) and propylene glycol increase the flexibility and elongation of the PHBV blends (Jost and Langowski, 2015). Addition of plasticizers promotes a decrease in both the glass transition temperature and the melting temperature. This allows processing at lower temperatures thus reducing the risk of thermal degradation. The presence of functionalized vegetable oil plasticizers increased PHBV ductility while its brittleness is noticeably reduced as a consequence of lower degree of crystallinity (Seydibeyoğlu et al., 2010). Epoxidized vegetable oils such as epoxidized linseed oil and epoxidized soybean oil are a sustainable and environmentally friendly alternative to petroleum-based conventional plasticizers (Garcia-Garcia et al., (2016). Other alternative studies in improving PHBV is the use of block copolymerization of PHBV using poly (butylene succinate), (PEG) and poly (L-lactic acid) (PLA) with the addition of dicumyl peroxide (DCP) to improve tensile toughness (Xiang et al., 2013).

Poly(caprolactone) (PCL), is a semi-crystalline linear aliphatic polyester derived from the ring opening polymerization of e-caprolactone, is also known to a biodegradable polymer. PCL is also a bio-compatible and non-toxic polyester that exhibit better mechanical strength (Lim, 2012). The low molecular weight PCL helps in improving the mechanical properties of polymer blends (Jenkins et al., 2007). PCL has low melting and glass transition temperature, which is around 60 °C and -60 °C. In contrast, the degradation temperature is around 350 °C, which is relatively high, and has greatest ductility properties with high elongation at break and modulus (Lovera et al., 2007). Previously there are several studies of PHBV/PCL blends using different method such as using electrospun (Bal et al., 2019) and solution casting (Chun and Kim, 2000). Different processing and preparation method give different end product (Ida et al., 2008).

Epoxidized palm oil (EPO) was used as plasticizers, which improved the properties of polymer blends (Silverajah et al., 2012a). According to Silverajah et. al (2012a), 1 wt.% of EPO is sufficient to improve the strength and the flexibility of neat PLA with significant increase in the thermal stability by 27 %. The oxirane rings in EPO is expected to react with polymers and helped in improving the toughness of the blends. To date, no study on the effect of EPO in PHBV/PCL blends can be found in literature to the best of author's knowledge. In this work, PHBV/PCL was prepared through melt blending method using an internal mixer. The tensile and impact properties were evaluated to identify a suitable PHBV/PCL proportion. Finally, the optimum PHBV/PCL blends were further improved with the presence of EPO as plasticizer. The effect of PCL content and 1 phr of EPO on mechanical and thermal properties of PHBV were studied in detail.

2. Experiments

2.1 Materials

Epoxidized palm oil (EPO) with 1.5 epoxide groups per triglyceride, 1,049 g/mol of molecular weight was obtained from Malaysian Palm Oil Board (MPOB). PHBV, grade Enmat Y1000P was purchased from TianAn Biopolymer, China in white powder form with average molecular weight of 283 x 10^3 g/mol, with density of 1.25 g/cm^3. PCL grade RJ-PCL with molecular weight of 60 x 10^3 g/mol was purchased from Hangzhou Ruijiang Chemical, China.

2.2 Preparation and characterizations

PHBV and PCL resins were dried in a vacuum oven at 40 °C for 24 h Weighted amount of 30 g of PHBV/PCL with various amount of PCL (0, 10, 20, 30, 40, 50 wt.%) were then prepared using melt mixing (internal mixer) at 175 °C for 10 min with slow rotation in order to avoid thermal degradation of PHBV. 60/40 PHBV/PCL were blended addition of 1 phr EPO.

Tensile test and impact test were performed to analyze the mechanical properties of PHBV/PCL blends. The sample were compressed at 175°C then were cut into dumbbell shape according to ASTM D638-5. The tensile properties such as~~,~~ tensile strength, Young's modulus and elongation at break were recorded. The rate used was 5 mm/min with 20 kN load. Seven specimens were tested and the average of the five best measurements were reported. The impact test specimens were notched using the notching machine to have uniform size of notching throughout the samples. Izod impact test was done in which the cracks propagated from tip to notch. This test was carried out according to ASTM D256 using Toyoseiki Izod Impact Tester with sample size 63.5 x 12.7 x 3 mm with a notch length of 2.54 mm.

Differential scanning calorimetry (DSC) is used to analyse the thermal properties of the blends. Perkin Elmer DSC 7 was used in this research. Small disk was used with 10 mg of sample and encapsulated in aluminium pans. High purity dry nitrogen was used as the inert atmosphere. The samples were heated from -20 °C to 190 °C at heating rate of 10 °C/min. DSC is also used to better understand the miscibility of these blends. The value of melting peaks (T_m) was recorded and analysed according to the graph of exothermic obtained. The degree of crystallinity, X_c was calculated using Eq (1), where ΔH_m is the melting enthalpy obtain from the endotherm, and ΔH_m^o is the melting enthalpy for 100 % crystalline PHBV, which is 146 J/g (Oliveira et al., 2007) and the *w* is the weight fraction of PHBV/PCL in the blend.

$$\%\, Crystallinity = \frac{\Delta H_m}{\Delta H_m^o} x\, \frac{100}{w} \qquad (1)$$

3. Results and discussion

Table 1 lists the DSC data of PHBV/PCL blends with varying composition. As seen in Table 1 individual PHBV showed T_m at 174 °C and individual PCL is around 64 °C. DSC of PHBV/PCL blends clearly show the immiscibility of these two biodegradable polymers, as indicated by two individual melting peaks located at typical temperature value of each melting point; one at about 170 °C attributable to PHBV and the other melt peak located at about 60 °C which is related to PCL melting temperature. The melting temperature of PHBV and PCL increase slightly compared to pure polymers and remained in the range of 174-178 °C for PHBV and almost same at 63 °C for PCL. This observation agrees with studies done by Lovera et al. (2007) and Furukawa et al. (2005) whereby the addition of PCL showed insignificant changes towards melting point the PHB. Microphase segregation is present in the melt state of the blends, which leads to the immiscibility of the blends.

Table 1: DSC data of PHBV/PCL blends

PHBV/PCL	PHBV			PCL		
	T_m (°C)	H_m (J/g)	Crystallinity Xc (%)	T_m (°C)	H_m (J/g)	Crystallinity Xc (%)
100/0	174	80.35	55.03	-	-	-
90/10	178	80.43	55.09	61	2.77	1.90
80/20	174	65.21	44.66	63	12.71	8.71
70/30	176	59.35	40.65	63	18.65	12.77
60/40	177	50.83	34.82	64	25.00	17.12
50/50	177	42.11	28.84	64	36.91	25.28
0/100	-	-	-	64	71.00	48.63
Plasticized 60/40	162	29.23	20.02	61	18.14	12.42

The melt enthalpy (H_m) for both polymers is obtained to calculate the crystallinity degree of each material in the blends. Crystallinity plays an important role in the mechanical properties of PHBV, PCL and their blends. The percentage crystallinity (Xc) of individual PHBV is about 55.03 % while the Xc of pure PCL is about 48.63 %. The addition of EPO deteriorated the T_m values of 60/40 PHBV/PCL blends from 177 °C to 162 °C and 64 °C to 61 °C. This is related to the formation of smaller and less-perfect crystals due to the addition of the plasticizers. There are two values of melting point which indicate the melting point of PHBV and PCL and the immiscibility of the plasticized 60/40 blends. However, there are significant changes whereby the range gap between PHBV and PCL for plasticized 60/40 are smaller compared to unplasticized (60/40) and moving near to each other. It can be concluded that addition of 1phr EPO into 60/40 blend improved the miscibility. The same observations of reduction in melting temperature have been reported by other authors in which epoxidized vegetable oil was used as plasticizer for PHBV (Slongo et al., 2018) and PLA (Awale et al., 2018).

The enthalpy of plasticized PHBV/PCL is smaller than unplasticized PHBV/PCL. The reduction in the fusion enthalpy results in a decrease in the crystallinity of the polymer blends. This is attributed by the increase of chain mobility. This trend is also seen in a previous study, in which the addition of EPO decreased the melting temperature as well as its crystallization phase of PLA (Chieng et al., 2014). Melting temperature of crystallizable polymer decreases as the concentration of non-crystallizable component increases (Han et al.,2013). The presence of EPO in the blend decreases the percentage of crystal which is Xc (unplasticized 60/40) = 34.82 to Xc (plasticized) = 20.02. Liu et al. (2017) observed distinctive morphologies under polarizing optical microscopy of plasticized and unplasticized PHBV/PCL due to different nucleation growth process in the presence of plasticizer and grafting agent. In PHBV, nucleus growth occurred over the central region and then spreads until the crystals cover the entire field of vision. However, the crystal nuclei of PCL are extremely small. The decrease in crystallinity is linked to the decrease in Young's modulus which will be discussed later. This differences in crystallinity leads to different in processing condition and different end-use properties (Shibata et al., 2005).

The tensile and impact properties of PHBV/PCL blends are listed in Table 2. Neat PHBV is known as brittle polymer with an elongation at break of approximately 7 %. The tensile strength and Young's modulus are approximately 21 MPa and 1,500 MPa. With regard to the tensile properties, individual PHBV can be classified as polymer with high tensile strength and modulus compared to pure PCL. Neat PCL showed lower tensile strength and Young' s modulus but higher elongation at break. In the presence of 10 wt.% of PCL, the tensile strength and Young's modulus of PHBV reduce to 18 MPa and 1,310 MPa before further reduction with addition of 30 wt.% of PCL. As the PCL content increases, both Young's modulus and tensile strength of PHBV decreased. In contrast, the elongation of break of PHBV is remarkably improved with addition of PCL. The elongation at break of PHBV/PCL blends improved almost 300 % in the presence of 40 wt.% PCL. The value of tensile strength, Young's modulus and elongation at break of the blends are in between the value of tensile strength of pure polymers.

Table 2: Tensile and impact properties of PHBV/PCL blends and plasticized PHBV/PCL blends

PHBV/PCL	Tensile Test			
	Tensile Strength (MPa)	Young Modulus (MPa)	Elongation at break (%)	Impact Strength (J/m)
100/0	20.7	1,467	7.2	23.1
90/10	18.5	1,310	15.4	24.3
80/20	18.2	1,240	19.3	27.0
70/30	14.3	690	35.1	27.3
60/40	12.3	630	37.5	28.5
50/50	11.4	580	37.0	29.3
0/100	10.5	350	52.5	35.2
Plasticized 60/40	14.5	580	39.0	29.4

The blend with 40 % PCL (60/40) showed the highest in elongation at break up to 37.5 %. The soft and flexible nature of PCL acts as impact modifier for rigid polymer as PHBV. Due to flexible nature of the PCL component, the tensile strength and modulus decrease to values of 12.3 MPa and 630 MPa. It is well known that miscibility and compatibility between 2 polymer matrices in blends allow a continuous phase and subsequently, load transfer between the phases is optimum (Smith and Verbeek, 2017). The incompatibility between PHBV and PCL reduced the tensile strength of the blends. Similarly reported by Arcana et al. (2007), the addition of PCL into polypropylene/PCL blends lowered the tensile strength of polypropylene.

The Izod impact strength of PHBV increases with increasing amount of PCL in the blends. A slight increase from 23 J/m (neat PHBV) up to 27 J/m was recorded in PHBV/PCL blends with 20 wt.% PCL and insignificantly increase from 20 wt.% of PCL to 50 wt.% of PCL (29 J/m). Impact strength is the ability of a material to absorb energy during fracture. PCL is able to absorb higher energy as compared to PHBV since PCL is ductile polymer. The evolution of the absorbed energy follows a similar tendency to that observed for elongation at break (Arcana et al., 2007). It can be concluded that the addition of PCL leads to an improvement in the ductile behavior of PHBV.

According to Ibrahim (2013), increases in impact strength are due to the state of dispersion, blend morphology, and/or other parameters on impact toughening of the blend. In this study, increasing PCL increase the dispersion area attached, which lead to an increment value of impact strength. During the impact test, PCL act as an absorber whereby it dissipates the energy resulted from the impact before the critical crack can propagate and improved the ability of the materials to withstand sudden forces.

The tensile strength of plasticized PHBV/PCL increase as much as 16 % higher than unplasticized PHBV/PCL. This indicates EPO acts as plasticizer which increase the interaction of PHBV and PCL and increase the flexibility of the blends. It is reported by Abdelwahab et al. (2012) reported that addition of plasticizer improved interfacial bonding of PHB and PLA. In other study, Silverajah et al. (2012b) reported that addition of 1 wt.% EPO improved the tensile strength of PLA up to 13 %. The elongation at break of the plasticized PHBV/PCL increases as compared to unplasticized PHBV/PCL. Addition of 1 phr EPO improved the ductility of PHBV/PCL blends. The Young's modulus decreases from 630 MPa to 580 MPa. The drop in tensile modulus showed that the EPO improves the flexibility of the blends and this can also be seen from the increment of elongation at break (37.5 to 39 %) and impact strength (28.5 to 29.4 J/m) of plasticized

PHBV/PCL. The presence of EPO increases the chain mobility of PHBV/PCL blends. This led to better extensibility of plasticized PHBV/PCL due to plasticizing effect and interaction between hydroxyl groups in biodegradable polymers with the epoxy group in EPO as suggested by Silverajah et al. (2012b). It was also reported that good interfacial adhesion between PLA and EPO increased the elongation at break, reaching 210 % with addition of 20 % EPO. This observation confirmed by good morphologies without the edge, cavity, and holes (Al-Mulla et al., 2010). Garcia-Garcia et al. (2016) found plasticized PHB has different behavior depending on the plasticizer type and content. An optimum amount of 10 phr epoxidized linseed oil increased the elongation at break of PHB up to 13.5 % from 9.7 % (unplasticized PHB) before the plasticizer saturation point was reached, which decreased the elongation at break with addition of 15 phr epoxidized linseed oil. On the other hand, increase in amount of epoxidized soybean oil in PHB decreased the elongation at break. In other study Hasan et al. (2019) reported the impact strength of PHB continues to decrease with increasing amount of liquid epoxidized natural rubber (LENR). The low molecular weight LENR was found to act as plasticizer instead of impact modifier for PHB.

4. Conclusions

The obtained result showed that PCL acts as an impact modifier and provides higher flexibility with a decrease in Young's modulus. As the PCL content in PHBV/PCL increased, the impact strength as well as elongation at break increased. The elongation at break rises from 7.2 % to 37 % as the PCL content increased. The tensile modulus decreases with increasing amount of PCL. The melting temperature of PHBV is in a range of 174 to 178 °C and melting temperature of PCL is almost the same at 63 °C. The crystallinity percentage of the blends decrease with increasing amount of PCL. DSC data confirmed that there are two different values for melting temperature with respect to PHBV and PCL, which indicate the immiscibility of the blend. At 60/40 blends ratio, the melting temperature decreased which widen the gap between the melting and degradation temperature of the blends. 60/40 blend ratio exhibits the highest elongation at break which showed better flexibility of the blends. The presence of EPO as plasticizer decreased the melting temperature of PHBV to 162 °C and also decreased crystallinity percentage. 1 phr of EPO also increased the impact, tensile strength and elongation and reduced the tensile modulus from 12.3 MPa to 14.5 MPa. Thus, it can be concluded that 1phr EPO increases the strength, flexibility, and toughness of PHBV/PCL blends. It is believed that this is due to plasticizing effect and interaction between hydroxyl groups in the PHBV/PCL blend with epoxy group in EPO.

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