

# The Effect of Poly(ethylene-octene) Grafted Maleic Anhydride Elastomer (POEgMA) and Liquid Epoxidised Natural Rubber (LENR) on Mechanical Properties of Poly(hydroxyl-3-butyrate) (PHB)

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Poly(hydroxyl-3-butyrate) (PHB) has a great potential in many applications due to its biodegradable and biocompatible properties. However, PHB is considered as a stiff material since it has high brittleness and narrow processing windows which limit the use of PHB. In order to improve the brittleness of PHB, poly(ethylene-octene) grafted maleic anhydride elastomer (POEgMA) and liquid epoxidized natural rubber (LENR) were incorporated into PHB using internal mixer. The blends were melt blended at temperature of 165 °C and rotor speed of 60 rpm for 8 min. The concentration of POEgMA and LENR were varied from 5, 10, 15 and 20 wt%. The mechanical and morphological properties were determined using tensile testing, Izod impact testing and scanning electron microscopy (SEM). Addition of 5 wt% POEgMA decreased the elongation at break and impact strength of PHB. The tensile strength and tensile modulus showed no significant changes with increasing amount of elastomers added to the blends. SEM micrograph revealed smaller rubber particles in the PHB/LENR system in comparison to the PHB/POEgMA blends at the same rubber concentration. The impact strength of PHB/LENR blends decreased significantly with the addition of elastomer. Thus based on this observation, it is suggested that the presence of LENR improves the plasticizing effect of the blends and not acting as an impact modifier.

## 1. Introduction

Plastics have been used widely around the world in various applications. However the plastics waste produced take long time to degrade thus cause land pollution and disrupt the ecological system. This issue has led to the increase of researches particularly in the field of environmentally friendly plastics. Poly(3-hydroxybutyrate) (PHB) is a thermoplastic polymer that is produced from renewable resources. Due to the biodegradability and environmentally friendly properties, PHB has become an interesting and significant material to be used in most industrial application such as packaging and commodity products. PHB is produced from microbial activity under nutrients-scarce conditions by acting as carbon and energy reserves for both non-sporulating and sporulating bacteria (Tan et al., 2014). PHB is a semi-crystalline polymer with melting temperature around 160-180 °C and degree of crystallinity of above 50 %. The tensile strength and tensile modulus of PHB are comparable to the properties of polypropylene (PP) (Somleva et al., 2013). However, the application of PHB is restricted because of its brittleness and low elongation at break. To date, various researches have been conducted to overcome these drawbacks such as modification via chemical functionalization and preparation of composites or blends with the addition of natural or synthetic sources to the polymers (Chee et al., 2018). Among these methods, blending PHB with rubber is the most effective and commonly used method in industry. Addition of rubber or elastomers in between of 5 to 25 wt% have been reported to toughen and improve the properties of brittle thermoplastics. The presence of this materials mainly act as stress concentrators and subsequently enhance the fractured energy absorption (Michler and Bucknall, 2001). Various rubber and elastomer such as amorphous ethylene-propylene rubber (EPR) (Abbate et. al., 1991), poly (vinyl acetate) (PVA) (Hay and Sharma, 2000),

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ethylene-propylene-diene terpolymer (EPDM) (Calvão et al., 2010) and poly(acrylonitrile-co-butadiene-co-styrene) (ABS) (de Carvalho et al., 2008) have been added to impart toughness to PHB.

Despite its advantages, most polymer blends are incompatible and have weak interfacial adhesion that lead to poor mechanical properties. Addition of compatibiliser is one of the efficient way to increase the effectiveness of rubber in toughening brittle polymers. Mohammad et al. (2017) incorporated two compatibilisers, maleated polylactic acid and maleated natural rubber to improve the adhesion between poly(lactic acid) (PLA) and natural rubber (NR). It was reported that, the presence of both compatibiliser increased the interfacial adhesion between PLA and NR which resulted in a more ductile PLA. Abbate et al. (1991) reported the incorporation of EPR grafted succinic anhydride group (EPR-g-SA) has increased the elongation at break of PHB from 1.5 to 6.5 % due to the chemical reactions that happened during the blending process. The anhydride functional groups of EPR-g-SA reacted with the ester functional group of PHB thus, improved the adhesion between the rubber and the matrix. Finer dispersion of rubber phase also achieved as a results of improved adhesion between rubber and matrix. Thus induced the yielding of toughened PHB and enhanced the capability of the materials to be plastically deformed. Poly(octene-ethylene) elastomer (POE) which was introduced by DuPont is a thermoplastic elastomers that have an excellent mechanical properties (Tang et al., 2011). POE have been used to improve the toughness of various polymers such as poly(ethylene terephthalate) (PET) (Chiu and Hsiao, 2005), PLA (Zhao et al., 2016) and others. In 2009, Su et al. (2009) reported, the addition of glycidyl methacrylate grafted poly(ethylene octane) (mPOE) in PLA has improved the impact strength of the blend by 7 folds. At 10 wt% of mPOE, the impact strength of the blend increased from 4 to 23.4 kJ/m<sup>2</sup> and continue to increase with increasing concentration of mPOE. It is suggested that the addition of mPOE improved the interfacial adhesion and reduced the surface tension between POE and PLA thus increased the toughness of the blends. The epoxy groups of the grafted polymers is believed to have reacted with carboxyl or hydroxyl groups of polyester hence enhance the adhesion between the blends (Su et al., 2009). Other than POEgMA, liquid epoxidised natural rubber (LENR) is another type of rubber that is currently getting significant attention to be used as toughening agent. LENR is a degraded form of epoxidised natural rubber (ENR), which turns into shorter chain due to the chain scission of the polyisoprene backbone. Natural rubber (NR) is one of the local sources that are inexpensive and easily access, thus it would be interesting to extend the use and consumption of this renewable material. However, NR has weak intermolecular forces which limited its application. Thus to improve the polarity of NR, polar epoxy groups was added to the C=C double bond of NR to obtain epoxidised natural rubber (ENR). In contrast to dried rubber, liquid rubber is advantageous for the production of various products due to the ease of processing and require less energy. Furthermore liquid rubber can be easily modified because of the low molecular weight and the presence of reactive groups which provide sites for the possibilities of chemical functionalisation. Kargarzadeh et al. (2015) used liquid natural rubber (LNR) and LENR to evaluate the effect of toughening agent on unsaturated polyester resins (UPR). It is observed that both liquid rubbers improved the impact strength of UPR with LENR showed a more significant improvement. Tan et al. (2013) reported that, the addition of 3 wt% of LENR increased the impact properties of epoxy matrix much higher in comparison to the addition of LNR at similar concentration. Thus it is proven that, LENR can be used as an effective toughening agent in improving the impact properties of epoxy. To the best of our knowledge, there is no study on mechanical properties of PHB with POEgMA or LENR has been reported so far. Thus, the aim of this paper is to investigate the mechanical properties such as tensile strength, Young's modulus, elongation at break and impact strength of PHB with the addition of various content of POEgMA and LENR.

## 2. Experiments

### 2.1 Materials

PHB, natural granule were supplied from Dalian Bate Import & Export Co. Ltd with the density of 1.28 g/cm<sup>3</sup> and melt flow index of 10 g/10min. The melting temperature of PHB is in between of 140-160 °C. The polyethylene-octene grafted Maleic Anhydride (POEgMA) (MN493) was produced from DuPont Packaging and Industrials Polymers with density of 0.87 g/cm<sup>3</sup> and melt flow index (190 °C/2.16 kg) of 1.6 g/10 min. Liquid epoxidised natural rubber (LENR) was acquired from Lembaga Getah Malaysia (LGM) and used as received.

### 2.2 Preparations and characterization

PHB and elastomers were melt blending in internal mixer (Brabender Plastograph EC, German) at 165 °C, with rotor speed of 50 rpm. PHB was blended for 2 min and then elastomers were added to the internal mixer, and both were mixed for another 8 min. The ratio of both elastomers added to PHB were varied at 5, 10, 15 and 20 wt%. The blended materials then compress by using compression moulding. The sample was preheated for 5 min then compressed for 7 min before cutting according to the standard test specimens.

Tensile testing was performed using Lloyd Universal Test Machine with 2.5 kN load, with the cross-head speed of 2 mm/min. The specimens were made according to ASTM D 638 in dumbbell shape. Data for tensile strength, tensile modulus and elongation at break were obtained from the stress-strain curve of the instrument's software's result.

To determine the impact strength of PHB/elastomers, samples were cut in rectangular bar according to ASTM D256 with dimension 3 (t) x 12.7 (l) x 3.3 (w) mm, minimum of 5 specimen for every testing. The notch was cut in 0.25 mm deep for the stress concentration area. The testing was conducted using Izod Toyoseiki with 11 J pendulum and notch is facing the edge of the pendulum.

The morphology of the fractured surface of PHB/elastomers blends were analysed using Hitachi Tm 3000 Tabletop microscope. All samples were sputtered coated with platinum for 30 s before examination.

### 3. Discussion

Table 1 shows the tensile strength of PHB and toughened PHB blends with the addition of POEgMA. From the table, the tensile strength of PHB is 17.80 MPa and the values remain unchanged when 5 and 10 wt% of POEgMA were added into the matrix. The tensile strength increases by 4%, from 17.38 to 18.11 MPa with the addition of 15 wt% of POEgMA. The value then decreases when 20 wt% of POEgMA was added. The decreasing of the tensile strength were also reported by Su et al. (2009) and Zhou et al. (2011). Su et al. (2009) have added POE and mPOE into PLA, and the tensile strength decreased when both elastomer added which due to the rubbery nature of the elastomer. In a study by Zhou et al. (2011), the tensile strength of PLA increased with the addition of 5 wt% of POE but then decreased when 20 wt% of POE was added. It was also reported that the high crystallinity of PLA played an important roles in determining the mechanical properties of the blends. The presence of 5wt% of POE increased the crystallinity of PLA as POE become the nucleation centre. Meanwhile, with the addition of POE-g-MAH, the tensile strength decreased steadily as compared to POE due to the good compatibility between PLA and POE-g-MAH that reduced the crystallinity of PLA.

Table 1 : Mechanical properties of PHB and toughened PHB

	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break, %	Impact strength (kJ/m <sup>2</sup> )
Notched				
PHB	17.80 ± 2.26	1420.27 ± 314.95	6.36 ± 0.23	11.89 ± 0.28
PHB/5% POEgMA	17.70 ± 3.55	1439.48 ± 136.23	3.48 ± 0.72	11.10 ± 0.94
PHB/10% POEgMA	17.38 ± 3.17	1390.94 ± 57.24	3.10 ± 0.34	11.52 ± 0.37
PHB/15% POEgMA	18.11 ± 2.31	1388.35 ± 142.42	3.48 ± 1.22	8.33 ± 0.51
PHB/20% POEgMA	16.54 ± 0.42	1356.29 ± 145.10	3.30 ± 0.89	9.76 ± 2.33
Unnotched				
PHB	-	-	-	12.07 ± 0.51
PHB/5% LENR	-	-	-	-
PHB/10% LENR	-	-	-	6.27 ± 1.20
PHB/15% LENR	-	-	-	6.15 ± 0.92
PHB/20% LENR	-	-	-	5.21 ± 1.01

The Young's modulus of PHB is listed in Table 1. From the table, the Young's modulus of PHB slightly increases by 1.35% from 1420.27 MPa to 1439.48 MPa when 5 wt% of POEgMA is added to the matrix. Subsequently, the Young's modulus of toughened PHB blends continue to decrease with increasing amount of POEgMA incorporated into the blends. Based on this observation it can be suggested that the Young's modulus of PHB blends remain unchanged regardless of the addition of POEgMA up to 20 wt%. Similar observation was reported by Calvão et al. (2012) which stated that, the modulus of PHB was not influenced by the amount of rubber added. The percentage of elongation at break showed a drop from 6.36% to 3.48%, nearly 45% with the addition of 5 wt% POEgMA. When the concentration of POEgMA increased to 10 wt%, the elongation at break continue to decrease to 3.10%. The elongation at break then increases when 15 wt% of POEgMA add to the matrix before decrease at 20 wt% of POEgMA. The decreasing of elongation at break were also observed by Pongtanayut et al. (2013) when 10 wt% of ENR added into PLA. As the rubber particle size increases, it will disrupt the discontinuity of PLA matrix thus affect the elongation at break. It was reported that, the ability of

rubber to elongate contributed by other factors such as mechanical properties of the matrix, type of rubbers, dispersion of the rubber and the size distribution of rubber within the matrix (Parulekar and Mohanty, 2006). The presence of POEgMA into PHB matrix was expected to improve the impact strength of PHB. However, from Table 1, the impact strength of PHB decreases by 6.64% when 5 wt% of POEgMA added into PHB, from 11.89 to 11.10 kJ/m<sup>2</sup>. Subsequent addition of more (10-20 wt%) POEgMA show a lower value of impact strength compare to pure PHB. The reason of the reduction in impact strength might be due to weak interaction between PHB and POEgMA as discussed later in taking into account the POEgMA particle size and the impact fracture surface morphology. Su et al. (2014) investigated the effect of maleic anhydride grafted POE (mPOE) and POE concentration on poly(ethylene terephthalate) (PET) toughening behaviour. It is found that extraordinary toughness can be attained by combination of good dispersion of rubber particles and appropriate interfacial adhesion condition. It is revealed from microscopic fractured morphology that moderate level of interfacial adhesion is important for good dispersion of rubber phase and debonding between PET matrix and rubber particles. The occurrence of matrix shear yielding can be easily attained under moderate level of interfacial adhesion thus dissipate more energy. Weak interfacial adhesion resulted in unstable cracking of PET and strong interfacial adhesion restricted interfacial debonding between PET matrix and POE. In a study by Calvão et al., (2012), the addition of 10 wt% of EPDM resulted in maximum increase of the impact strength of PHB. Further addition of rubber give no improvement to the impact strength of PHB/EPDM blends. In addition, de Carvalho et al. (2008) found that, at 10 and 20 wt% of ABS, the impact strength of PHB remained the similar until the concentration of ABS increased to 30 wt%.

The SEM micrographs of fractured PHB and toughened PHB surfaces from Izod impact test are shown in Figure 1. From Figure 1a, the surfaces of pure PHB reveals a smooth fractured surface indicated the typical fractured surface of a brittle materials. With the addition of POEgMA, there are two-phases of morphology observed where the rubbery phase dispersed in PHB matrix. At 5 wt% of POEgMA (Figure 1b), it can be seen that there are voids on the fractured surface of the matrix with the elastomer dispersed in droplets shape. The average size of the droplets were in between of 5.36  $\mu\text{m}$  to 5.71  $\mu\text{m}$ . The presence of voids on the PHB matrix might due to the rubber pulled out, indicating the weak interaction between POEgMA and PHB. Furthermore, there are gaps around the rubber particles as shown by the arrow in Figure 1b with no significant signs of plastic deformation. From the observation, it can be suggested that the rubber acts more like a cavity in controlling the premature crack growth. With more rubber added into the matrix, the particles size remains unchanged and it seems to act as stress-raisers and unable to act efficiently as sites termination due to the weak interaction between PHB and POEgMA. Therefore, only small amount of energy can be dissipated during the fracture. This observation is in agreement with the obtained impact strength of PHB and POEgMA blends discussed earlier. Su et al. (2014) reported that addition of small amount of mPOE (between 3-5 wt%) reduced the elastomer particles size to from 6  $\mu\text{m}$  to 2.5  $\mu\text{m}$ .

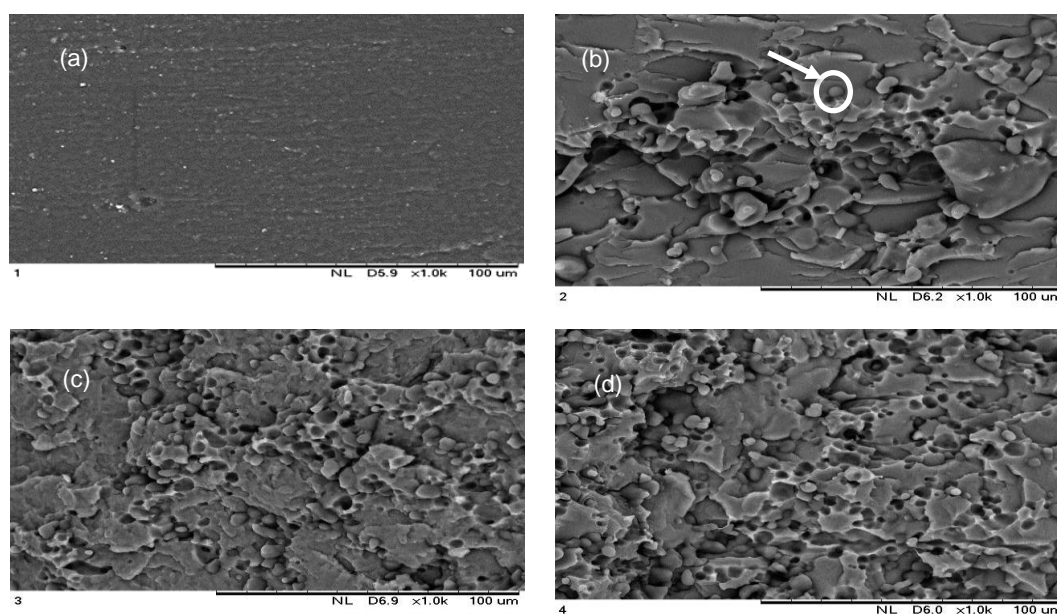


Figure 1: SEM image of PHB and PHB with POE : (a) PHB, (b) PHB/5 wt% POE, (c) PHB/10 wt% POE and (d) PHB/15 wt% POE

The effect of adding different amounts of LENR amount on the impact strength of PHB was analyzed using un-notched impact Izod tester. However, due to the brittleness of PHB with 5 wt% of LENR, the value was unable to be determined and discussed in this study as the sample failed during analysis. From Table 1, the impact strength of PHB decreases by almost half of the initial value with the addition of 10 wt% of LENR. The impact strength of PHB continues to decrease with increasing amount of LENR. This observation might be attributed to the plasticising effect of the LENR, instead of forming a phase-separated particle. As can be seen from the SEM micrograph in Figure 2, the voids/holes presence in the matrix are much smaller compared to the voids presence in PHB matrix in Figure 1. The same observation was reported by Kargarzadeh et al. (2015) and Bijarimi et al. (2014). LENR has a lower molecular weight and viscosity than PHB, which explain the small size of the holes presented in the blends. The size of the LENR in the matrix remains unchanged with increasing amount of LENR. Kargarzadeh et al. (2015), found that at the concentration of above 6 wt%, LENR was observed to be dissolved in the unsaturated polyester (UPR). Therefore LENR could not function as impact modifier. Similar observation by Bijarimi et al. (2014) reported that the addition of 10 wt% of LENR acted as a plasticiser instead of a compatibiliser in a system based on PLA and natural rubber.

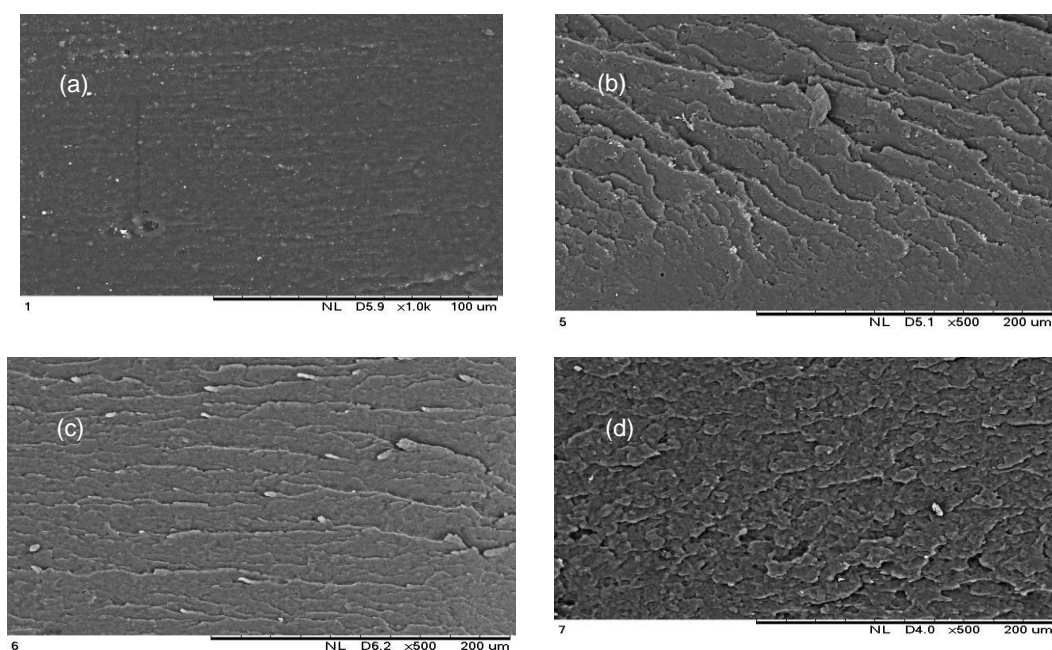


Figure 2: SEM image of PHB with LENR : (a) PHB, (b) PHB/5 wt% LENR, (c) PHB/10 wt% LENR and (d) PHB/15 wt% LENR

#### 4. Conclusions

In this study, POEgMA and LENR were used to improve the brittleness of PHB. The tensile strength and Young's modulus of PHB shows no significant improvement with the increasing amount of POEgMA up to 20 wt%. The impact strength of PHB decreased with the incorporation of POEgMA. From the SEM micrographs, rubber pulled out can be seen clearly which indicate the weak interaction between POEgMA and PHB. In the system containing LENR, the impact strength of PHB decreased almost half of the initial value when 10 wt% of LENR was added into PHB. SEM micrographs of the fractured samples showed the presence of LENR droplets in the matrix at 5 wt%. As the higher amount of LENR was added into PHB, the micrographs revealed a smoother surface suggesting the miscibility of LENR into the matrix. Thus it can be concluded that the addition of LENR acted as plasticiser instead of an efficient impact modifier.

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